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# Influences upon the Lead Isotopic Composition of Organic and Mineral Horizons in Soil Profiles from the National Soil Inventory of Scotland (2007-09)

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4 **Influences upon the Lead Isotopic Composition of Organic and**

5 **Mineral Horizons in Soil Profiles from the National Soil**

6 **Inventory of Scotland (2007-09)**

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10 **John G. Farmer<sup>a\*</sup>, Margaret C. Graham<sup>a</sup>, Lorna J. Eades<sup>b</sup>, Allan Lilly<sup>c</sup>, Jeffrey R.**

11 **Bacon<sup>c</sup>**

12

13 <sup>a</sup>School of GeoSciences, The University of Edinburgh, Crew Building, Alexander Crum

14 Brown Road, Edinburgh, EH9 3FF, Scotland, UK

15 <sup>b</sup>School of Chemistry, The University of Edinburgh, Joseph Black Building, David Brewster

16 Road, Edinburgh EH9 3FJ, Scotland, UK

17 <sup>c</sup>James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, Scotland, UK

18

19

20

21 \*Corresponding author. Tel.: +44-131-6504907; fax: +44-131-6620478

22 *E-mail address:* [J.G.Farmer@ed.ac.uk](mailto:J.G.Farmer@ed.ac.uk) (J.G. Farmer)

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## Abstract

Some 644 individual soil horizons from 169 sites in Scotland were analysed for Pb concentration and isotopic composition. There were three scenarios: (i) 36 sites where both top and bottom (i.e. lowest sampled) soil horizons were classified as organic in nature, (ii) 67 with an organic top but mineral bottom soil horizon, and (iii) 66 where both top and bottom soil horizons were mineral. Lead concentrations were greater in the top horizon relative to the bottom horizon in all but a few cases. The top horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio was lesser (outside analytical error) than the corresponding bottom horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio at (i) 64%, (ii) 94% and (iii) 73% of sites, and greater at only (i) 8%, (ii) 3% and (iii) 8% of sites. A plot of  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios showed that the Pb in organic top (i, ii) and bottom (i) horizons was consistent with atmospherically deposited Pb of anthropogenic origin. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the organic top horizon in (ii) was unrelated to the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the mineral bottom horizon as demonstrated by the geographical variation in the negative shift in the ratio, a result of differences in the mineral horizon values arising from the greater influence of radiogenic Pb in the north. In (iii), the lesser values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the mineral top horizon relative to the mineral bottom horizon were consistent with the presence of anthropogenic Pb, in addition to indigenous Pb, in the former. Mean anthropogenic Pb inventories of 1.5 and 4.5 g m<sup>-2</sup> were obtained for the northern and southern halves of Scotland, respectively, consistent with long-range atmospheric transport of anthropogenic Pb (mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ~1.16). For cultivated agricultural soils (Ap), this corresponded to about half of the total Pb inventory in the top 30 cm of the soil column.

Keywords: Pb, isotope ratios, organic soil, mineral soil, Scotland

## 1. Introduction

Clair Patterson's finding in the 1960s that more than 90% of the atmospheric Pb in the northern hemisphere at that time was derived from anthropogenic sources such as car-exhaust emissions (in the era of leaded petrol), coal combustion and metal ore smelting (Patterson, 1965; Murozumi et al., 1969) has subsequently been supported by many historical studies based on the Pb analysis of cores from ice sheets, peat bogs and lake sediments (e.g. Boutron et al., 1991; Shotyk et al., 1998; Renberg et al., 2001). Such studies have often included Pb isotope analyses, which have provided valuable information on the relative contributions of Pb from sources of differing Pb isotopic composition associated with various human activities over the past few thousand years (e.g. Shirahata et al., 1980; Rosman et al., 1997; Bindler, 2011). Based partly on the isotopic evidence (e.g.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios), it is widely accepted that accumulations of Pb in ice, peat and sediment cores are anthropogenic in origin and that they are the result of long-term and long-range atmospheric deposition (e.g. Steinnes et al., 2005a; Zheng et al., 2007; Steinnes, 2009; Klaminder et al., 2011).

In Scotland, there have been numerous studies of the isotopic composition of sources of Pb (Sugden et al., 1993; Farmer et al., 1999, 2000) and of Pb in peat, lake sediments, moss and other terrestrial plants in the rural environment (e.g. Farmer et al., 1996, 1997, 2002, 2010, 2015; MacKenzie et al., 1997, 1998; Eades et al., 2002; Weiss et al., 2002; Patrick and Farmer, 2007; Cloy et al., 2008; Kylander et al., 2009). With the exception of a few studies on urban and suburban soils (e.g. Farmer et al., 2011; MacKinnon et al., 2011), most Pb isotopic work on Scottish soils has focussed on the rural environment, in particular at the Glensaugh field station and long-term monitoring site in the rural north east (e.g. Bacon et al., 1992, 1995, 2004, 2006). Data for organic soils at Glensaugh, which is a site distant from any point sources, show typical  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios to be 1.15-1.17 in surface horizons but 1.18-

1.20 in deeper horizons (Bacon et al., 1992, 1995, 2004, 2006; Farmer et al., 2005). Long-range atmospheric transport and deposition of Pb has been invoked in explanation, with contributory sources including car-exhaust emissions ( $^{206}\text{Pb}/^{207}\text{Pb}$  ratio  $\sim 1.08$ ), Pb ore smelting ( $\sim 1.17$ ) and coal combustion ( $\sim 1.18$ ) (Farmer et al., 1999, 2000, 2010). Hilltop peat cores at Glensaugh have shown anthropogenic Pb inventories in the range  $6\text{--}9\text{ g m}^{-2}$ , with  $\sim 40\%$  deposited prior to 1900 and a further  $\sim 20\%$  between 1900 and 1930 from ore smelting/coal combustion during the UK industrial era, prior to the introduction of leaded petrol, which was in use in the UK until its total ban in 2000 (Farmer et al., 2005).

There is, however, an alternative view that there is little evidence for long-range atmospheric transport of Pb. While conceding the influence of human activities in and around urban centres, a few large-scale soil surveys in both Europe and North America have concluded that soil Pb contamination results principally from local point sources with only minimal influence of long-range atmospheric transport (Reimann et al., 2009, 2011, 2012). One such study provided Pb isotope data for European cultivated agricultural soils (Ap, 0-20 cm) that included  $\sim 50$  soils for the whole of Scotland, collected on a 50 km grid (Reimann et al., 2012).

The National Soil Inventory of Scotland (NSIS) was recently resampled on a 20 km grid and samples taken from a range of soil horizons and depths. This exercise has provided an ideal opportunity to carry out a much more detailed and systematic survey of the Pb status of Scottish soils, in particular of the Pb isotope composition, to investigate the geographical spread, extent and source of Pb contamination in Scotland. A similar country-wide survey has recently been carried out in The Netherlands, where Walraven et al. (2013a, 2013b) concluded that the Pb isotope composition of the additional Pb in  $\sim 350$  rural topsoils (A, 0-20 cm) differed clearly from lithologically inherited Pb, as observed in the corresponding subsoils (BC, C, 100-120 cm), and argued for an anthropogenic origin.

The specific objectives of this project were to (i) determine the Pb isotopic composition of soil profiles for which Pb concentrations had been measured as part of the recent NSIS 2007-09 Survey, (ii) establish the baseline Pb isotope composition of mineral soils and the potentially anthropogenically influenced Pb isotope composition of both mineral and organic soil horizons throughout Scotland, (iii) compare the Pb isotope composition of surface soil horizons with that of bottom (i.e. lowest sampled) soil horizons and (iv) assess the causes and extent of any observed variations in Pb isotope composition, including the magnitude of the potential anthropogenic contribution.

## **2. Materials and Methods**

### *2.1 National Soil Inventory of Scotland (NSIS)*

The National Soil Inventory of Scotland (NSIS) consists of samples taken on a regular grid pattern in 1978-88 (NSIS 1) and resampled in 2007-09 (NSIS 2). The grid was aligned with the Ordnance Survey (OS) National Grid and 183 soil profiles were sampled between 2007 and 2009 at 20 km spacing. Fig. 1 shows the distribution among the OS zones (i.e. 100 km grid squares) of the 169 soil profiles on which this paper was ultimately based.

### *2.2 Sampling*

At each location a soil pit, rectangular in shape and sufficiently large to allow sampling of each of the major horizons, was dug by spade to a depth of at least 75 cm. This was sufficient to allow the description and sampling of the parent material at each location, where possible. Supplementary Information (SI) Table 1 summarises the main soil groups and the

number of soil horizons for the sites in each OS zone. A description of the different soil horizons is given in SI Table 2.

Approximately 1-1.5 kg of relatively stone-free soil was collected from each horizon. Samples were generally taken from a 10-cm depth band situated approximately in the middle of the horizon or at depths thought to be appropriate where the thickness of the horizon was judged to warrant more than one sample. In some situations where the horizon thickness was less than 10 cm, the top and bottom sample depths were set to allow a representative and pure sample to be collected from the horizon. Thin transition zones up to 6 cm thick were generally excluded where boundaries were gradual or diffuse.

The soil material was loosened and extracted using a trowel or knife, collected in a sampling tray held level with the lower boundary of the sample depth, and placed in a low density polyethylene bag. In general, soils were sampled sequentially beginning with the lowest horizon.

## *2.3 Sample preparation and analysis*

### *2.3.1 Acid digestion*

Soil samples were air-dried at 30°C and sieved (<2 mm). Ground soil samples (<2 mm, 0.25-5 g) were initially moistened with ~0.5-1 mL of deionised (UHP) water and then digested in a mixture of HCl and HNO<sub>3</sub> (*aqua regia*, 3:1) under reflux for 2 h (ISO 11466, 1995). If the samples contained >0.5 g organic C, an additional 1 mL HNO<sub>3</sub> was added before digestion for every 0.1 g C above 0.5 g until the reaction stopped and all organic C had been oxidised. In addition, organic samples were left to pre-digest prior to the reflux digestion, typically for 16-20 h.

The digest was allowed to cool, filtered and made up to a known volume with 0.5 M HNO<sub>3</sub> for analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

### *2.3.2 Pb concentration by ICP-MS (James Hutton Institute)*

Lead concentrations were determined by ICP-MS using the pulse count mode of an Agilent 7500ce instrument with octopole reaction system and nickel cones (Agilent Technologies, Stockport, UK). The RF forward power was 1500 W, with argon gas flows of 0.9 and 0.1 L min<sup>-1</sup> for carrier and makeup flows, respectively. All sample solutions were diluted with high-purity water (18.2 MΩ cm) from a Milli-Q water system (Millipore, Watford, UK) in line using the Agilent ISIS system with a ratio of 1:10 and subsequently nebulised using a Babington nebuliser. The spectrum analysis acquisition mode was used, with three points per unit mass and integration times of 1 s per point for each of <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb, and three replicate runs per sample. Quantification of Pb was based on summation of counts per second from all three measured isotopes for sample and Pb standard solutions, with <sup>185</sup>Re employed as the internal standard during instrumental analysis. Quality Control solutions were run at a frequency of every 20 samples to evaluate instrument performance, with digest test soils regularly analysed within sample sets to ensure digest quality.

An in-house test sample of a mineral soil ('Analytical Top Soil') with indicative Pb concentration ( $\pm 1$  standard deviation (s.d.)) of  $42.3 \pm 3.0$  mg kg<sup>-1</sup> (n=1430) was included in each batch of samples and put through the complete analytical procedure including *aqua regia* extraction and ICP-MS analysis. The measured Pb concentration ( $\pm 1$  s.d.) of this test soil over the three years of the NSIS 2 project was  $43.2 \pm 2.7$  mg kg<sup>-1</sup> (n=197).

### *2.3.3 Pb isotope ratios by ICP-MS (University of Edinburgh)*



Soil digest solutions were diluted to a Pb concentration of  $<25 \mu\text{g L}^{-1}$  with high-purity water (18.2 M $\Omega$  cm) from a Milli-Q water system (Millipore, Watford, UK). Lead isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) were then determined by quadrupole ICP-MS using the pulse count mode of an Agilent 7500ce instrument with octopole reaction system and nickel cones (Agilent Technologies, Stockport, UK). The RF forward power was 1540 W and the reflected power 1 W. The argon gas flows were 0.82 and 0.20 L min $^{-1}$  for carrier and makeup flows, respectively, and the peristaltic pumping rates into the Mira mist nebuliser 0.2 or 1.2 L min $^{-1}$ , respectively. The isotope analysis acquisition mode was used, with three points per unit mass and integration times of 0.3 s per point for each of  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ , and six replicate runs per sample. A Pb isotopic reference material from the National Institute of Standards and Technology (NIST), SRM 981, was used for mass bias correction.

Mean analytical errors (1 s.d.) on  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios in the soil samples (n=674) were  $\pm 0.004$ ,  $\pm 0.008$  and  $\pm 0.007$ , respectively. Overall mean analytical precision for Pb isotope ratio determination in duplicate soil sample solutions (n=63) averaged  $\pm 0.3\%$ . The mean isotope ratios ( $\pm 1$  s.d.) of  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  determined in the in-house ‘Analytical Top Soil’ (n=12) as  $1.174 \pm 0.004$ ,  $2.459 \pm 0.005$  and  $2.095 \pm 0.007$ , respectively, were in good agreement with previously established values of  $1.175 \pm 0.001$ ,  $2.451 \pm 0.001$  and  $2.087 \pm 0.002$ . For NIST SRM 1643e Water Reference Material (n=49), used to check the consistency of inter-batch analytical runs, mean values of  $1.167 \pm 0.003$ ,  $2.450 \pm 0.005$  and  $2.099 \pm 0.004$  were obtained for  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ , respectively.

### 3. Results and Discussion

Of the 183 sites of NSIS 2, there were 175 for which material from at least two different soil horizons was available and for which both Pb concentration and Pb isotope ratios were obtained. Of these 175 sites, six were considered anomalous by virtue of an unusually high ( $\geq 1.44$ ) or unusually low ( $\leq 1.10$ ) value of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio determined in the lowest sampled horizon of the soil profile. Consequently, they are considered separately, leaving 169 sites for the bulk of this study (Fig. 1).

### *3.1 Soil Profiles of Pb concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio*

Figs. 2a-e present a typical Pb concentration and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio profile for each of five different categories of soil horizon sequences (cf. SI Table 2 for soil horizon descriptions) based upon the nature of the uppermost and lowermost sampled soil horizon. The categories were: (i) organic-organic (36 sites) (Fig. 2a), (ii) organic-mineral (67 sites) (Fig. 2b), (iii) organic-mineral for OS zone NH, where the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the lowermost mineral horizon was often high (up to 1.35) (Fig. 2c), (iv) mineral (Ap)-mineral (42 sites) (Fig. 2d) and (v) mineral (non-Ap)-mineral (24 sites) (Fig. 2e). There were 66 mineral-mineral sites in total. The predominant trends at the 169 sites of all five categories were of (i) decreasing Pb concentration (usually from the top soil horizon but occasionally (~15%) from the second top horizon) with increasing depth and (ii) increasing  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio with increasing depth. Of the 169 sites there were only 10 (i.e. 6%) where the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the top soil horizon was greater (outside 1 s.d. analytical error) than that of the corresponding bottom horizon, compared with 134 (i.e. 79%) where it was lesser. The extent of the difference in individual cases, however, depended upon which combination of organic or mineral uppermost and lowermost soil horizons pertained and, indeed, upon factors such as geographical variation in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the lowermost soil horizon when it was mineral in nature (cf. Figs. 2a-

e). The SI Figs. 1-6 provide six examples of each case including the six anomalous sites, an example of which is shown in Fig. 2f.

### *3.2 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and Pb concentrations in top and bottom soil horizons*

Fig. 3 presents histograms of the number of sites with values of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios, ranging by 0.01 increment from 1.10 to 1.36, corresponding to the three scenarios of top and bottom soil horizon being organic and organic (Fig. 3a), organic and mineral (Fig. 3b) and mineral and mineral (Fig. 3c). Fig. 4 displays separate histograms of Pb concentrations for organic top, organic bottom, mineral top and mineral bottom soil horizons at all sites as appropriate. Individual horizons are considered in turn below.

#### *3.2.1 Mineral bottom soil horizon*

Of the 169 sites, there were 133 where the bottom soil horizon was classified as mineral (A-1, E-3, B-22, BC-35, C-72). The mean mineral bottom horizon depth range was 56-78 cm, with a mean sample depth range of 65-75 cm.

##### *3.2.1.1 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios*

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ranged from 1.132 to 1.348 (Figs. 3b,c) with a mean value of 1.208 (median 1.196). The different main mineral bottom soil horizons (B, BC, C) exhibited similar mean and median values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (Table 1).

There was, however, considerable geographical variation across Scotland, as shown by consideration of values in each of the OS zones (SI Table 3). For example, of the 19 sites with a mineral bottom  $^{206}\text{Pb}/^{207}\text{Pb}$  value  $\geq 1.25$  (Fig. 3), eight were from NH (four  $\geq 1.30$ ), four from NN (one  $\geq 1.30$ ), two from NJ and one from each of NM (one  $\geq 1.30$ ) and NR.

Excluding the Orkney and Shetland Islands (n=3), there appeared to be two main areas (n=117), consisting of contiguous zonal groupings. In the first of these, comprising the six zones NG, NH, NJ, NM, NN, NR (Fig. 1), where the mean values for the mineral bottom soil horizons of the individual zones ranged from 1.201 (NM) to 1.257 (NH) (Fig. 5a, SI Table 3), the overall mean value for the sites in the group (n=64) was  $1.227 \pm 0.048$  (median 1.225). In the second grouping, comprising the five zones NO, NS, NT, NX, NY (Fig. 1), where the mean values for the mineral bottom soil horizons of the individual zones ranged from 1.180 (NY) to 1.196 (NT) (Fig. 5a, SI Table 3), the overall mean value for the sites in the group (n=53) was  $1.189 \pm 0.018$  (median 1.187). A third grouping comprised the rest of the zones in the north and lay on the fringes of the first main grouping, i.e. NF, NB, NC, ND, NK (Fig. 1). The mean values for the mineral bottom soil horizons of the individual zones in this third grouping ranged from 1.177 (NC) to 1.211 (ND) (Fig. 5a, SI Table 3), with an overall mean value (n=13) of  $1.188 \pm 0.037$  (median 1.176).

The rock types of stones in the 19 mineral bottom soils which had  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios  $\geq 1.25$  were predominantly granite or schists (e.g. quartz-mica schists). The typically greater values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the bottom mineral soils of the NG, NH, NJ, NM, NN, NR group compared with the rest of Scotland are attributable to the accumulation of radiogenic Pb in these soils resulting from the radioactive decay of  $^{238}\text{U}$  (half-life =  $4.47 \times 10^9$  years and  $^{235}\text{U}$  (half-life =  $0.70 \times 10^9$  years) present in uraniferous minerals in these soils, in addition to primordial Pb. Values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio as high as 1.35-1.39 have been found in bottom sediments of freshwater lakes in the granitic terrain of the Cairngorm and Grampian Mountains (Yang et al., 2007; Farmer et al., 2015), which are located primarily in OS zones NH, NJ, NN and upper NO.

### 3.2.1.2 Pb concentrations

The mean Pb concentration (range 1.3-133 mg kg<sup>-1</sup>, n=133) for the mineral bottom soil horizon (Fig. 4d) was 13 (median 9.1) mg kg<sup>-1</sup>, with similar mean and median values for the different main mineral bottom soil horizons (Table 1).

In contrast to the <sup>206</sup>Pb/<sup>207</sup>Pb results, there did not appear to be much geographical variation in Pb concentration across Scotland as demonstrated by mean and median values for individual OS zones with n≥10 (Fig. 6a, SI Table 4). Furthermore, of the 15 sites with a mineral bottom Pb concentration ≥20 mg kg<sup>-1</sup> (Fig. 4), one was from NC, two from ND, one from NH, one from NK (one ≥100 mg kg<sup>-1</sup>), one from NM, two from NN, two from NO (one ≥100 mg kg<sup>-1</sup>), one from NR, one from NS and three from NT. In the first grouping (NG, NH, NJ, NM, NN, NR, n=64), established above as having an elevated mean <sup>206</sup>Pb/<sup>207</sup>Pb ratio of 1.227 (median 1.225), the mean Pb concentration was 9.9 (median 7.9) mg kg<sup>-1</sup>. In the second grouping (NO, NS, NT, NX, NY, n=53), for which the mean <sup>206</sup>Pb/<sup>207</sup>Pb ratio was 1.189 (median 1.187), the mean Pb concentration was 14 (median 10) mg kg<sup>-1</sup> [12 (median 10) mg kg<sup>-1</sup> when one value of 121 was excluded]. In the third grouping comprising the rest (NF, NB, NC, ND, NK, n=13), but excluding the Orkney and Shetland Islands, the mean Pb concentration was 23 (median 8.9) mg kg<sup>-1</sup> [14 (median 8.5) mg kg<sup>-1</sup> when one value of 133 was excluded].

### 3.2.2 Mineral top soil horizon

Of the 169 sites, there were 66 where the uppermost soil horizon was classified as mineral (Ap-42, uncultivated A-21, E-1, B-2). The mean mineral uppermost soil horizon depth range for all A (n=63) was 0-25 cm with a mean sample depth range of 6.2-15.8 cm. For cultivated Ap horizons, the corresponding mean ranges were 0-29 cm and 6.9-16.9 cm; for other A, they were 1-18 cm and 4.7-13.6 cm; and, overall (n=66), the mean ranges were 1-26 cm and 6.9-16.6 cm.

### 3.2.2.1 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ranged from 1.153 to 1.236 (Fig. 3c) with a mean value of 1.176 (median 1.174), with similar corresponding mean values for all A uppermost horizon samples (n=63) and their sub-sets Ap (n=42) and other A (n=21) (Table 1).

There appeared to be some geographical variation, as shown by consideration of values for the OS zones (Fig. 5b, SI Table 3). For example, of the eight sites with a mineral uppermost horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  value  $\geq 1.19$  (Fig. 3), five were from NJ (two  $\geq 1.20$ ), one from HY (one  $\geq 1.20$ ), one from ND and one from NH. Excluding the Orkney and Shetland Islands (n=2) and combining the two most northerly contiguous zones established for the mineral bottom soil horizon, i.e. NF, NB, NC, ND, NK (n=3) and NG, NH, NJ, NM, NN, NR (n=23), where the mean values for the mineral top soil horizons of the individual zones ranged from 1.169 (NK) to 1.195 (ND) (Fig. 5b, SI Table 3), the overall mean value for the group (n=26) was  $1.183 \pm 0.018$  (median 1.179). In the second grouping, the most southerly contiguous zones established for the mineral bottom soil horizon, i.e. the five zones NO, NS, NT, NX, NY (n=38), where the mean and median values for the mineral top soil horizons of individual zones ranged from 1.165 (NS) to 1.175 (NT) (Fig. 5b, SI Table 3), the overall mean value for the group (n=38) was  $1.171 \pm 0.007$  (median 1.172). Alternatively, taking the northernmost zones as HU, HY, NB, NC, ND, NF, NG, NH, NJ, NK, the mean  $^{206}\text{Pb}/^{207}\text{Pb}$  value (n=19) was  $1.188 \pm 0.017$  (median 1.184) (mean sample mid-point depth = 11.8 cm) compared with a mean value (n=47) of  $1.172 \pm 0.010$  (median 1.172) for the southernmost zones NM, NN, NO, NR, NS, NT, NX, NY (mean sample mid-point depth = 11.7 cm).

### 3.2.2.2 Pb concentrations

The mean Pb concentration (range 3.5-329 mg kg<sup>-1</sup>, n=66) for the mineral top soil horizon (Fig. 4c) was 41 (median 27) mg kg<sup>-1</sup>, with similar mean and median values for the different main mineral top soil horizons of all A, Ap and other A (Table 1).

As with the <sup>206</sup>Pb/<sup>207</sup>Pb results, there appeared to be some geographical variation, as shown by consideration of values for the OS zones (Fig. 6b, SI Table 4). Only 11% (2/19) of samples from the northernmost OS zones of HU, HY, NB, NC, ND, NF, NG, NH, NJ, NK (mean 39 ± 74 mg kg<sup>-1</sup> [or 22 ± 23 mg kg<sup>-1</sup> when one value of 329 mg kg<sup>-1</sup> was excluded], median 17 mg kg<sup>-1</sup>) had Pb concentration ≥ 50 mg kg<sup>-1</sup>, compared with 28% (13/47) for the southernmost zones NM, NN, NO, NR, NS, NT, NX, NY (mean 42 ± 34 mg kg<sup>-1</sup>, median 30 mg kg<sup>-1</sup>).

### 3.2.3 Organic top soil horizon

Of the 169 sites, there were 103 where the uppermost soil horizon was classified as organic (LF, F, LFH, FH - 24 in all; H-10; O-69). The mean organic top soil horizon depth range was 0-6 cm for LF, F, LFH, FH, 3-11 cm for H and 2-19 cm for O, with corresponding mean sample depth ranges of 0.9-5.7 cm, 3.8-9.7 cm and 5.6-14.5 cm, respectively. Overall, the mean organic top horizon soil depth range was 1.4-15.3 cm, with a mean organic top soil sample depth range of 4.3-12.0 cm.

#### 3.2.3.1 <sup>206</sup>Pb/<sup>207</sup>Pb ratios

The <sup>206</sup>Pb/<sup>207</sup>Pb ratio ranged from 1.105 to 1.202 (Figs. 3a,b) with a mean value of 1.156 (median 1.159) and mean values for the different organic top soil horizons of 1.135 (median 1.136) for LF, F, LFH, FH, 1.154 (median 1.154) for H and 1.163 (median 1.164) for O (Table 1). With respect to O top samples from different depths, the mean <sup>206</sup>Pb/<sup>207</sup>Pb value

where the mid-point of sample depth was  $\leq 4$  cm (n=8) was  $1.147 \pm 0.013$ ;  $\leq 10$  cm (n=47)  $1.161 \pm 0.013$ ;  $>10$  cm (n=22)  $1.167 \pm 0.006$ ;  $\geq 18$  cm (n=7)  $1.170 \pm 0.006$ .

Although at first glance there appeared to be some geographical variation across Scotland, on the basis of mean organic top soil horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  values for the OS zones, ranging from 1.130 (NK) and 1.139 (NO) to 1.164 (ND) and 1.171 (NS) (Fig. 5c, SI Table 5), this was largely explicable on the basis of the nature of the organic top soil horizon sampled and the mean sample depth. For example, 83% of NO samples were LF-H (i.e. non-O) and the mean sample depth (n=6) was 4.6 cm. The zones with the next lowest mean  $^{206}\text{Pb}/^{207}\text{Pb}$  values (1.142-1.160) were NJ, NH, NN, NT and NM, with mean sample depths of 7.1, 5.6, 6.2, 6.4 and 5.3 cm, respectively, and to which LF-H horizons contributed 75, 44, 41, 56 and 33% of samples, respectively. In contrast, 0% of NS samples (mean 1.171) were LF-H and the mean sample depth (n=5) was 16.2 cm. The zones (excluding HY and HU for Orkney and Shetland) with the next highest mean  $^{206}\text{Pb}/^{207}\text{Pb}$  values (1.163-1.164) were ND, NR, NX, NB and NC, with mean sample depths of 12.8, 9.9, 16.3, 9.1 and 11.1 cm, respectively, and to which LF-H horizons contributed 0, 25, 25, 0 and 0% of samples, respectively. The zone with the lowest mean  $^{206}\text{Pb}/^{207}\text{Pb}$  value, NK (1.130) had a mean sample depth (O horizon) of just 2.5 cm.

### 3.2.3.2 Pb concentrations

The mean Pb concentration (range 4.3-580 mg kg<sup>-1</sup>, n=103) for the organic top soil horizon (Fig. 4a) was 77 (median 43) mg kg<sup>-1</sup> (Table 1), with mean values (mg kg<sup>-1</sup>) for the different organic top soil horizons of 57 (median 43) for LF, F, LFH, FH, 102 (median 52) for H and 80 (median 42) for O (Table 1).

In contrast to the  $^{206}\text{Pb}/^{207}\text{Pb}$  results, there did appear to be considerable systematic geographical variation, north to south, in the Pb concentration data (Fig. 6c, SI Table 4). Only



5.5% (3/55) of samples from the northernmost OS zones of HU, HY, NB, NC, ND, NF, NG, NH, NJ, NK (mean  $38 \pm 32 \text{ mg kg}^{-1}$ , median  $32 \text{ mg kg}^{-1}$ ) had concentrations  $\geq 100 \text{ mg kg}^{-1}$ , compared with 27% (7/26) from the more centrally located zones NM, NN, NO (mean  $113 \pm 135 \text{ mg kg}^{-1}$ , median  $63 \text{ mg kg}^{-1}$ ) and 50% (11/22) from the southernmost zones NR, NS, NT, NX (mean  $133 \pm 99 \text{ mg kg}^{-1}$ , median  $109 \text{ mg kg}^{-1}$ ).

### 3.2.4 Organic bottom horizon

Of the 169 sites, there were 36 where the bottom soil horizon was classified as organic (O-36). The mean organic bottom soil horizon depth range was 43-90 cm with a corresponding mean sample depth range of 61-72 cm.

#### 3.2.4.1 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ranged from 1.135 to 1.226 (Fig. 3a), with a mean value of 1.175 (median 1.177) (Table 1). For samples taken from profiles with O bottom horizons, the mean  $^{206}\text{Pb}/^{207}\text{Pb}$  value was  $1.172 \pm 0.017$ ,  $1.181 \pm 0.019$  (or  $1.174 \pm 0.011$  when two values of 1.216 and 1.226 were excluded) and  $1.171 \pm 0.017$  for samples with mid-point sample depths of  $<50 \text{ cm}$  ( $n=9$ ),  $50\text{-}79 \text{ cm}$  ( $n=15$ ) and  $\geq 80 \text{ cm}$  ( $n=12$ ), respectively.

On the basis of mean organic bottom soil horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  values for individual OS zones, there appeared to be little geographical variation (Fig. 5d, SI Table 5). The mean  $^{206}\text{Pb}/^{207}\text{Pb}$  values for the northernmost zones of HU, NB, NC, ND, NF, NG, NH, NJ ( $n=20$ ) of  $1.176 \pm 0.022$  (median 1.178) (or  $1.171 \pm 0.016$  (median 1.176) when two values of 1.216 and 1.226 were excluded) were comparable with the mean value of  $1.174 \pm 0.012$  (median 1.177) for the southernmost zones of NM, NN, NO, NR, NS, NT, NX ( $n=16$ ).

#### 3.2.4.2 Pb concentrations

The mean Pb concentration (range 1.4-36 mg kg<sup>-1</sup>, n=36) for the organic bottom soil horizon (Fig. 4b) was 7.5 (median 4.3) mg kg<sup>-1</sup> (Table 1). In contrast to the <sup>206</sup>Pb/<sup>207</sup>Pb results, there did appear to be considerable systematic geographical variation, north to south, in the Pb concentration data (Fig. 6d, SI Table 4). None (0/20) of the samples from the northernmost OS zones of HU, NB, NC, ND, NF, NG, NH, NJ (mean 3.8 ± 1.8 mg kg<sup>-1</sup>, median 3.25 mg kg<sup>-1</sup>) had concentrations > 8 mg kg<sup>-1</sup>, compared with 50% (8/16) from the southernmost zones of NM, NN, NO, NR, NS, NT, NX (mean 12 ± 10 mg kg<sup>-1</sup>, median 7.6 mg kg<sup>-1</sup>).

### *3.3 Comparison of top and bottom soil horizon <sup>206</sup>Pb/<sup>207</sup>Pb ratios*

#### *3.3.1 Organic top and organic bottom soil horizons*

Of the 36 sites with an organic top and organic bottom soil horizon, the Pb concentration was always greater in the former (Fig. 7). There were 23 sites (i.e. 64%) where the top <sup>206</sup>Pb/<sup>207</sup>Pb ratio was lesser (outside 1 s.d. analytical error) than that of the bottom horizon and only three (i.e. 8%) where the latter was lesser (outside 1 s.d.) than the former, the other 10 (i.e. 28%) having top and bottom horizon values within 1 s.d. of each other (Fig. 7). This is also reflected in Table 2, which shows the mean values by OS zone of corresponding top and bottom <sup>206</sup>Pb/<sup>207</sup>Pb ratios and the mean difference between the paired <sup>206</sup>Pb/<sup>207</sup>Pb ratios of the two horizons. The overall mean difference (top minus bottom) for the 36 sites was -0.014 (Table 2).

The finding of increasing <sup>206</sup>Pb/<sup>207</sup>Pb ratios with increasing depth in organic soils such as peat is in line with established trends in cores from ombrotrophic peat bogs from around Scotland (Farmer et al. 1997; MacKenzie et al. 1997, 1998; Cloy et al., 2008) and reflects temporal changes in sources of anthropogenic Pb deposited from the atmosphere, as shown in the plot of <sup>208</sup>Pb/<sup>207</sup>Pb vs. <sup>206</sup>Pb/<sup>207</sup>Pb (Fig. 8). The more recent influence of car-exhaust

emissions, containing Pb from leaded petrol (to which Australian Pb of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ~1.04 was a major contributor), relative to Pb from Scottish ore mining/smelting and coal burning can be clearly seen in the organic top horizon. The best-fit lines through the organic top and organic bottom data, however, are of similar gradient, 1.047 and 1.010, respectively (Fig. 8).

### 3.3.2 Organic top and mineral bottom soil horizons

Of the 67 sites with an organic top and mineral bottom soil horizon, the Pb concentration was greater in the former in all but five (two outside analytical error) cases (Fig. 9), although the direct comparison of concentrations is of rather limited value in view of the approximately order of magnitude difference in dry bulk density between these two horizons. There were 63 sites (i.e. 94%) where the top horizon  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio was lesser (outside 1 s.d. analytical error) than the bottom horizon value and only two (i.e. 3%) where the latter was lesser (outside 1 s.d.) than the former, the other two (i.e. 3%) having top and bottom horizon values within 1 s.d. of each other (Fig. 9). This is also reflected in Table 3, which shows the mean values by OS zone of corresponding top and bottom  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and the mean difference between the paired  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the two horizons. The overall mean difference for the 67 sites was -0.066 (Table 3), but the magnitude varied noticeably with OS zone. Those with the greatest mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the mineral bottom horizon, e.g. NG, NH, NJ, NN and NR (Fig. 5a, SI Table 3), had the largest mean differences of -0.064, -0.109, -0.080, -0.077 and -0.089, respectively, between the paired  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for the organic top and mineral bottom horizon (Table 3). Indeed, when the mean differences were computed for the three distinct OS zone groupings established in 3.2.1.1, the  $-0.084 \pm 0.052$  for NG, NH, NJ, NM, NN and NR (n=41) was much greater than the  $-0.045 \pm 0.023$  for NO, NS, NT, NX and NY (n=15) and  $-0.028 \pm 0.040$  for NF, NB, NC, ND, NK (n=10). In contrast, the

corresponding mean differences in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio between organic top and organic bottom horizons for these three zonal groupings were very similar at  $-0.015 \pm 0.014$  ( $n=12$ ),  $-0.018 \pm 0.017$  ( $n=9$ ) and  $-0.014 \pm 0.023$  ( $n=14$ ), respectively.

The plot of  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  (Fig. 10) again demonstrates the influence of anthropogenic sources of Pb upon the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the organic top horizon Pb (cf. Fig. 8). Indeed the equation for the best-fit line through the organic top horizon data in Fig. 10 ( $^{208}\text{Pb}/^{207}\text{Pb} = 1.223 + 1.050 \ ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.939$ ) is near-identical to that in Fig. 8 ( $^{208}\text{Pb}/^{207}\text{Pb} = 1.227 + 1.047 \ ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.899$ ) and differs from the corresponding best-fit line ( $^{208}\text{Pb}/^{207}\text{Pb} = 1.436 + 0.883 \ ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.697$ ) through the mineral bottom data.

Fig. 9 also shows quite clearly the lack of relationship between the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of organic top and mineral bottom horizons, although there is a tendency for some of the values to be closer in magnitude when the mineral bottom horizon is A, E or B, i.e. perhaps in receipt of some downwardly transported anthropogenic Pb (cf. 3.3.4).

### 3.3.3 Mineral top and mineral bottom soil horizons

Of the 66 sites with a mineral top and mineral bottom soil horizon, the Pb concentration was greater in the former in all but five (two outside analytical error) cases (Fig. 11). There were 48 (i.e. 73%) where the top  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio was lesser (outside 1 s.d. analytical error) than the bottom value and only five (i.e. 8%) where the latter was lesser (outside 1 s.d.) than the former, the other 13 (i.e. 20%) having top and bottom horizon values within 1 s.d. of each other (Fig. 11). This is reflected in Table 4, which shows the mean values by OS zone of corresponding top and bottom  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and the mean difference between the paired  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the two horizons. The overall mean difference for the 66 sites was -0.021, but the magnitude varied noticeably with OS zone (Table 4). Those with the highest mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the mineral bottom horizon, e.g. NG, NH, NJ and NM (cf. Fig. 5a,

SI Table 3), had the largest mean differences of -0.033, -0.050, -0.029 and -0.040, respectively, between the paired  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for the mineral top and mineral bottom horizon (Table 4). Indeed, when the mean differences were computed for the three distinct OS zone groupings established in 3.2.1.1, the  $-0.029 \pm 0.031$  for NG, NH, NJ, NM, NN and NR (n=23) was greater than the  $-0.015 \pm 0.012$  for NO, NS, NT, NX and NY (n=38) and  $-0.007 \pm 0.022$  for NF, NB, NC, ND, NK (n=3), although much less than the corresponding differences for the sites with organic top and mineral bottom soil horizons (cf. 3.3.2). This can be attributed to (i) the presence in the mineral top horizon of some indigenous Pb in the mineral lattice of greater  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio than the anthropogenic Pb deposited from the atmosphere which constitutes the Pb in the organic horizons and (ii) the preponderance of samples from NO, NS, NT, NX and NY (38/66, i.e. 58%), which have a lesser mean mineral bottom  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (cf. Table 4), in the mineral top and mineral bottom scenario than is the case in the organic top and mineral bottom scenario where samples from NG, NH, NJ, NM, NN and NR (41/66, i.e. 62%) predominate (cf. Table 3).

The plot of  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  (Fig. 12) shows the influence of anthropogenic Pb upon the gradient (0.763) in the mineral top horizon when compared with the gradient (0.644) for the mineral bottom horizon data.

### 3.3.4 Intermediate horizons

For those sites where the A horizon was above only two other soil horizons (n=29), the mean difference between the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the A and middle horizon was  $-0.020 \pm 0.015$ , with the A value lesser (outside 1 s.d. analytical error) in 83% of cases. In contrast, the value for the middle horizon was within 1 s.d. of the value for the bottom horizon in 69% of cases, with only a further 14% lesser and 17% greater and an overall mean difference of  $0.000 \pm 0.009$ . In profiles with four sampled horizons (n=23), the mean differences between the

$^{206}\text{Pb}/^{207}\text{Pb}$  ratios for A-second, second-third and third-bottom horizons were  $-0.017 \pm 0.019$ ,  $-0.002 \pm 0.017$  and  $-0.001 \pm 0.008$ , respectively.

For comparison, the sites where there was an organic horizon (not necessarily the uppermost organic horizon) directly above at least three mineral horizons ( $n=42$ ) were divided into two groups based upon the range of values of the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for the lowermost mineral horizon: (i)  $<1.200$ , (ii)  $\geq 1.200$ . In scenario (i) ( $n=20$ ), the mean differences between the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for organic-second, second-third and third-bottom horizons were  $-0.017 \pm 0.016$ ,  $-0.007 \pm 0.011$  and  $-0.001 \pm 0.007$ , respectively. In scenario (ii) ( $n=22$ ), the corresponding mean differences were  $-0.043 \pm 0.020$ ,  $-0.018 \pm 0.022$  and  $-0.008 \pm 0.015$ , respectively. The larger differences in scenario (ii) reflect the greater bottom  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, which directly influences the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of the second and third (both mineral) horizons and makes it easier to discern some downward transport of anthropogenic Pb (of much lower  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio) from the organic and second (predominantly E, eluvial) horizons to the third (B) horizon (cf. 3.3.2, Fig. 9). Transport of anthropogenic Pb from organic soil horizons to mineral soil horizons has been well documented elsewhere. This may be substantial, as reported for forest floors in the north-eastern USA (Miller and Friedland, 1994; Kaste et al., 2003; Richardson et al., 2014) and Scandinavia (Brännvall et al., 2001; Steinnes and Friedland, 2005; Steinnes et al., 2005b), less so for Mediterranean (Teutsch et al., 2001) and Dutch (Walraven et al., 2014) roadside soils and to only a very limited extent in the peaty topsoils of the intensively studied small organic-rich upland catchment at Glensaugh, Scotland (Vinogradoff et al., 2005; Bacon et al., 2006; Graham et al., 2006).

### *3.4 Anthropogenic Pb inventories*

519 Anthropogenic Pb inventories were calculated for each site. Each sample Pb concentration  
520 was extrapolated to the whole of the appropriate horizon and the depth interval and dry bulk  
521 density used to convert concentration ( $\text{mg kg}^{-1}$ ) to inventory ( $\text{g m}^{-2}$ ). All Pb in the organic  
522 horizons (L, F, H, O) was taken to be anthropogenic. For mineral horizons, a correction to the  
523 measured concentration was made for 'baseline' Pb, taken to be the Pb concentration in the  
524 lowermost mineral horizon. Excluding seven sites ( $17\text{--}68 \text{ g m}^{-2}$ , mean  $32 \pm 18 \text{ g m}^{-2}$ ) where  
525 the anthropogenic Pb inventory was  $>15 \text{ g m}^{-2}$ , the mean value for each OS zone is listed in  
526 SI Table 6 and displayed in Fig. 13.

527 The range of mean values for each OS zone from HU to NM was  $0.6\text{--}2.2 \text{ g m}^{-2}$ , with an  
528 overall average of  $1.5 \pm 1.2 \text{ g m}^{-2}$ , sites with organic ( $n=58$ ), Ap ( $n=13$ ) and A ( $n=8$ ) top  
529 horizons exhibiting comparable mean values of  $1.5 \pm 1.2$ ,  $1.7 \pm 1.7$  and  $1.2 \pm 0.7 \text{ g m}^{-2}$ ,  
530 respectively. Cloy et al. (2008) reported  $1.2 \text{ g m}^{-2}$  (post-1800 AD) for a dated peat core  
531 collected in 2004 from Turclossie Moss (OS zone NJ).

532 For the remaining zones, NN-NY, the range of mean values was  $3.3\text{--}6.2 \text{ g m}^{-2}$ , with an  
533 overall average of  $4.5 \pm 3.0 \text{ g m}^{-2}$ . The sites with organic ( $n=44$ ), Ap ( $n=24$ ) and A ( $n=15$ ) top  
534 horizons were again in good agreement at  $4.5 \pm 3.3$ ,  $4.6 \pm 3.0$  and  $4.2 \pm 0.7 \text{ g m}^{-2}$ ,  
535 respectively. For dated peat cores collected in the 21<sup>st</sup> century, Farmer et al. (2015) reported  
536  $3.70 \text{ g m}^{-2}$  (post-1610 AD) for Great Moss (NN), while Cloy et al. (2008) found  $2.1\text{--}3.6 \text{ g m}^{-2}$   
537 (post-1800 AD) for Flanders Moss (NS),  $2.5\text{--}4.3 \text{ g m}^{-2}$  (post-1800 AD) for the Red Moss of  
538 Balerno (NT) and  $2.7\text{--}5.0 \text{ g m}^{-2}$  (post-1800 AD) for Carsegowan Moss (NX).

539 Considering all sites with mineral top horizons together ( $n=60$ , i.e. excluding six sites  
540  $>15 \text{ g m}^{-2}$ ), the anthropogenic Pb accounted for 43% and 56% of the total Pb inventories for  
541 HU-NM and NN-NY, respectively, to the depth of anthropogenic Pb penetration (mean  $\sim 30$   
542 cm) as determined by consideration of Pb concentration and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in each soil  
543 profile. The mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio calculated for anthropogenic Pb at such sites in HU-NM

and NN-NY was  $1.158 \pm 0.019$  and  $1.161 \pm 0.014$ , respectively, with an overall average value of  $1.160 \pm 0.016$ , in good agreement with the mean value of  $1.164 \pm 0.012$  established for total anthropogenic Pb at sites (excluding one site  $>15 \text{ g m}^{-2}$ ) with organic top horizons. Taking these mineral top and organic top horizon sites together, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of anthropogenic Pb lay between 1.140 and 1.179 at 89% of sites.

Similarly, for sites with a specifically Ap mineral top horizon (i.e. excluding six sites  $>15 \text{ g m}^{-2}$ ), the anthropogenic Pb accounted for 36% (HU-NM) and 51% (NN-NY) of the total Pb inventories to a mean depth of  $\sim 30 \text{ cm}$  and had a calculated mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of  $1.159 \pm 0.018$ . So far as Scotland is concerned, therefore, these findings are contrary to the conclusion of Reimann et al. (2012) that the atmospheric Pb contamination of the northern hemisphere as demonstrated using ice cores, lake sediments or peat bogs contributes little to the total Pb inventory of European agricultural soils.

### *3.5 Anomalous sites*

#### *3.5.1 Unusual $^{206}\text{Pb}/^{207}\text{Pb}$ profiles*

The very high value (1.576) of the organic bottom horizon (Oa2)  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for Uist (NF) (SI Fig. 6a) was probably the result of the inclusion of some mineral dust (of high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio) in the bottom horizon, as the value of the dry bulk density was  $0.813 \text{ g cm}^{-3}$ , some 4-5 times greater than the corresponding values for the three overlying horizons, Os1, Os2 and Oa1.

The very high value (1.441) of the mineral bottom horizon (Bh)  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for South Culblean Hill (NJ) (SI Fig. 6b), which is in the eastern Grampian Mountains where the underlying rock is granite, almost certainly resulted from the presence of radiogenic Pb elevated in  $^{206}\text{Pb}$  relative to  $^{207}\text{Pb}$ , as found elsewhere in the north in this study (cf. Figs. 3c,



5, SI Fig. 3), a view supported by the high, but less extreme, value of 1.342 for the overlying E(h) horizon (SI Fig. 6b).

At the other four sites – Lewis (NB), Skye (NG), Lochan na Bearta (NH) and Mull (NM) (SI Figs. 6c-f) – the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio uncharacteristically declined from top to bottom horizon, to values of 1.077 (Oa2), 1.050 (BCg), 1.100 (BC) and 1.043 (Ah), respectively. These sites are in NW Scotland and, although not characteristic in general of  $^{206}\text{Pb}/^{207}\text{Pb}$  profiles there, could perhaps be indicative of local effects of mineralisation or contamination.

That such apparently anomalous values as those above can occur is supported by the findings of a recent regional-scale geochemical survey of soil O and C horizon samples in Nord-Trondelag, Central Norway (Reimann et al., 2015). There,  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in the O horizon as low as 1.0399, compared with a median value of 1.1512 for O horizon samples and with minimum and maximum values for C horizon samples of 1.0658 and 1.9630, respectively, were reported.

### 3.5.2 Large anthropogenic Pb inventories

The large estimated anthropogenic Pb inventories ( $>15 \text{ g m}^{-2}$ ) not included in the calculation of mean inventories for individual OS zones (Fig. 13, SI Table 6) related, with one exception (NN, Bruach Burn, Oa,  $24.2 \text{ g m}^{-2}$ ), to sites with uppermost Ap horizons, i.e. Rhum (NG,  $18.3 \text{ g m}^{-2}$ ), Kincardine (NJ, 67.6), Arbirlot (NO, 21.8), Pappert (NS, 42.9), Borrowstoun (NT, 29.8) and Heathhall 85 (NY, 17.3). The average anthropogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for these Ap sites was  $1.169 \pm 0.007$ . Apart from Bruach Burn, the organic sites with the largest estimated anthropogenic Pb inventories were Meluncart (NO,  $10.6 \text{ g m}^{-2}$ ), Stobieside (NS, 13.9), Caddonhead (NT, 10.7), Forest of Ae (NT, 10.1) and Wood of Auchleand (NX, 14.0). The site vegetation included from *Sphagnum* moss peat bogs to heather moors and coniferous woodlands. The average anthropogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for these six sites was  $1.166 \pm 0.012$

( $1.170 \pm 0.006$ , excluding Caddonhead), very similar to the six Ap sites of elevated anthropogenic Pb inventory. Meluncart (NO,  $10.6 \text{ g m}^{-2}$ ) is very close to the long-term monitoring station at Glensaugh (NO), for which a mean value of  $7.4 \pm 1.5 \text{ g m}^{-2}$  (range 6-9  $\text{g m}^{-2}$ ) was recorded for four hilltop peat cores (Farmer et al., 2005). On the basis of the inventory of naturally occurring radioactive  $^{210}\text{Pb}$ , it has been suggested that this could be an area of enhanced deposition of Pb as a result of occult deposition at altitude. Elsewhere, factors such as enhanced trapping, e.g. by the leaves of trees, and subsequent leaf fall could contribute to elevated inventories of Pb in forests. More generally, variations in deposition efficiency might also be expected as a result of site topography relative to prevailing wind direction.

#### **4. Conclusions**

The measurement of Pb isotopic composition in 644 samples from individual horizons of 169 soil profiles for which Pb concentrations had previously been determined as part of the National Soil Inventory of Scotland (2007-09) established the following:

- (i) the Pb isotope composition of mineral bottom soils (i.e. the lowest sampled mineral horizons) varied geographically and was especially influenced by the presence, in more northerly soils on granitic rocks, of radiogenic Pb that resulted in greater  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of up to 1.35 compared with typical values of 1.17-1.20 in more southerly soils;
- (ii) the Pb isotope composition of both organic top soil horizons and organic bottom soil horizons (i.e. the lowest sampled organic horizons) was consistent with past atmospheric deposition of Pb from a range of anthropogenic emission sources;

- (iii) the lesser  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and greater Pb concentrations of organic top soil horizons bore no relation to those of underlying mineral bottom soil horizons (i.e. the lowest sampled mineral horizons);
- (iv) the lesser  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios but greater Pb concentrations of mineral top soil horizons relative to mineral bottom soil horizons (i.e. the lowest sampled mineral horizons) were consistent with the presence of additional anthropogenic Pb;
- (v) based on calculations using measured Pb concentrations and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for the soil profiles, the estimated anthropogenic Pb soil inventory was found to vary geographically from an average of  $4.5 \text{ g m}^{-2}$  in the south to  $1.5 \text{ g m}^{-2}$  in the north, comparable to values previously determined for ombrotrophic peat bogs and freshwater lake sediments and indicative of long-range atmospheric transport;
- (vi) anthropogenic Pb accounted for ~50% of the total Pb inventory to a depth of ~30 cm in cultivated agricultural soils (Ap).

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## FIGURE LEGENDS

Figure 1. Map of Scotland with the Ordnance Survey (OS) National Grid imposed and the corresponding diagrammatic version showing the distribution among individual OS zones of the 169 soil profile sites considered in this study.

Figure 2. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (closed circle) vs soil horizon and depth: (a) Forest of Ae (OS zone NT), organic top to organic bottom; (b) Balhomish (NO), organic top to mineral bottom; (c) Drumguish (NH), organic top to mineral bottom (of high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio); (d) Balcalk (NO), Ap mineral top to mineral bottom; (e) Chanlock (NS), A mineral top to mineral bottom; (f) Mull (NM), organic top to mineral bottom (anomalous site).

Figure 3. Histograms of number of samples with  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in 0.01 intervals from 1.10-1.36 for three scenarios: (a) organic top horizon with organic bottom horizon; (b) organic top with mineral bottom; (c) mineral top with mineral bottom.

Figure 4. Histograms of number of samples with Pb concentrations in 10 mg kg<sup>-1</sup> intervals (0-90 mg kg<sup>-1</sup>) and 100 mg kg<sup>-1</sup> intervals (100-600 mg kg<sup>-1</sup>) for (a) organic top, (b) organic bottom, (c) mineral top and (d) mineral bottom horizons.

Figure 5. Diagrammatic OS National Grid Maps of Scotland showing mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio by OS zone for (a) mineral bottom, (b) mineral top, (c) organic top and (d) organic bottom horizons.

Figure 6. Diagrammatic OS National Grid Maps of Scotland showing mean Pb concentration by OS zone for (a) mineral bottom, (b) mineral top, (c) organic top and (d) organic bottom horizons.

Figure 7. Plots of Pb concentration (logarithmic scale) and of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, organic bottom horizon vs organic top horizon (for paired samples, n=36)

Figure 8. Plots of  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio vs  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for organic top and organic bottom horizons (for paired samples, n=35, i.e. excluding Aisir (NC)). The best-fit line through the organic top data (n=35) is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.227 + 1.047 ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.899$ ; and through the organic bottom data (n=32, i.e. excluding two Lewis (NB) and one Uist (NF) samples) is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.274 + 1.010 ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.621$ ). Mean isotopic ratio values, with 1 s.d. error bars, are shown for leaded petrol (circle), Wanlockhead Pb (inverted triangle) ore and UK coal (square) (cf. Farmer et al., 1999, 2000).

Figure 9. Plots of Pb concentration (logarithmic scale) and of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, mineral bottom horizon vs organic top horizon (for paired samples, n=67). Closed circles represent mineral bottom samples from A, E and B horizons and open circles from BC and C horizons.

Figure 10. Plots of  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio vs  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for organic top (shown on two scales for  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio) and mineral bottom horizons (for paired samples, n=67). The best-fit line through the organic top data is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.223 + 1.050 ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.939$ ; and through the mineral bottom data is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.436 + 0.883 ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.697$ . Mean isotopic ratio values, with 1 s.d. error bars, are shown for leaded petrol (circle), Wanlockhead Pb ore (inverted triangle) and UK coal (square) (cf. Farmer et al., 1999, 2000).

Figure 11. Plots of Pb concentration (logarithmic scale) and of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, mineral bottom horizon vs mineral top horizon (for paired samples, n=66). Closed circles represent mineral top samples from E and B horizons and open circles from A horizons.

Figure 12. Plots of  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio vs  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio for mineral top and mineral bottom horizons (for paired samples, n=65, i.e. excluding Torridon (NG)). The best-fit line through the mineral top data is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.563 + 0.763 \ ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.523$ ; and that through the mineral bottom data is  $^{208}\text{Pb}/^{207}\text{Pb} = 1.723 + 0.644 \ ^{206}\text{Pb}/^{207}\text{Pb}$ ,  $r^2=0.505$ .

Figure 13. Diagrammatic OS National Grid Map of Scotland showing the mean anthropogenic Pb inventory ( $\text{g m}^{-2}$ ) by OS zone.

## SUPPLEMENTARY INFORMATION (SI)

### SI FIGURE LEGENDS

SI Figure 1. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (closed circle) vs soil horizon and depth for organic top to organic bottom sites: (a) Sallachy (OS zone NC), (b) Dalganachan (ND), (c) Strathrusdale (NH), (d) Fealar Lodge (NO), (e) Loch Lyon (NN), (f) Forest of Ae (NT).

SI Figure 2. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (closed circle) vs soil horizon and depth for organic top to mineral bottom sites: (a) Langwell Ullapool (OS zone NC), (b) Kintessack (NJ), (c) Mid-Lorn (NN), (d) Edradour (NO), (e) Wormsleuch (NT), (f) Balhomish (NO).

SI Figure 3. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (closed circle) vs soil horizon and depth for organic top to mineral bottom (of high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio) sites (all OS zone NH): (a) Strathbran, (b) Garve, (c) Attadale, (d) Dochfour, (e) North Lochaber, (f) Drumguish.

SI Figure 4. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (closed circle) vs soil horizon and depth for Ap mineral top to mineral bottom sites: (a) Findon (OS zone NH), (b) Kincardine (NJ), (c) Westpark (NS), (d) Balcalk (NO), (e) Silverburn (NT), (f) Shawhill (NY).

923 SI Figure 5. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio  
924 (closed circle) vs soil horizon and depth for A mineral top to mineral bottom sites: (a)  
925 Bohally Wood (OS zone NN), (b) Keig (NJ), (c) Chanlock (NS), (d) Langhope (NT), (e)  
926 Glenlee (NX), (f) Craigton Row (NX).

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928 SI Figure 6. Six selected profiles of Pb concentration (open circle) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio  
929 (closed circle) vs soil horizon and depth for six anomalous sites, all with organic top: (a) Uist  
930 (OS zone NF), organic bottom; (b) S. Culblean Hill (NJ), (c) Lewis (NB), (d) Skye (NG), (e)  
931 Mull (NM), (f) Lochan na Bearta (NH).

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